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Modelling of gas–liquid reactors – stability and dynamic behaviour of gas–liquid mass transfer accompanied by irreversible reaction

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Abstract

The dynamic behaviour and stability of single-phase reacting systems has been investigated thoroughly in the past and design rules for stable operation are available from literature. The dynamic behaviour of gas–liquid processes is considerably more complex and has received relatively little attention. General design rules for stable operation are not available. A rigorous gas–liquid reactor model is used to demonstrate the possible existence of dynamic instability (limit cycles) in gas–liquid processes. The model is also used to demonstrate that the design rules of Vleeschhouwer, Garton and Fortuin, Chemical Engineering Science, 47, 1992, 2547–2552, are restricted to a specific limit case. A new approximate model is presented which after implementation in bifurcation software packages can be used to obtain general applicable design rules for stable operation of ideally stirred gas–liquid reactors. The rigorous reactor model and the approximate design rules cover the whole range from kinetics controlled to mass transfer controlled systems and are powerful tools for designing gas–liquid reactors.

Keywords: Gas–liquid reactor model; Dynamic stability; Limit cycle; Perturbation analysis; Hopf bifurcation; Design rules

1. Introduction

1.1. Single-phase systems

Multiplicity, stability and dynamic behaviour of single-phase reacting systems have been investigated intensively in the past. During the last 50 years a lot of papers have been devoted to this subject. Most papers (Bilous & Amundson, 1955; Aris & Amundson, 1958; Uppal, Ray & Poore, 1974,1976; Olsen & Epstein, 1993) deal with purely theoretical treatment of multiplicity and stability in single-phase reactors, while other papers (Baccaro, Gaitonde & Douglas, 1970; Vejtasa & Schmitz, 1970; Vleeschhouwer & Fortuin, 1990; Heiszwolf & Fortuin, 1997) discuss both experimental and theoretical work.

From all these papers one general and important conclusion can be drawn: whenever a system can be described sufficiently accurate by two ordinary differential equations (ODEs) with respect to time (one heat and one material balance, like an irreversible single-phase first-order reaction in a CISTR reactor), the occurrence of instability is easily predicted by analysing the characteristics of the linearised system of equations for process conditions in the neighbourhood of the steady state.

1.2. Gas–liquid systems

Prediction of the dynamic behaviour of gas–liquid two phase reactors is usually more complex, since these systems involve: (1) more than two component balances, i.e. ODEs and (2) mass transfer between the gas and the liquid phase.

In literature only a few papers (Hoffman, Sharma & Luss, 1975; Sharma, Hoffman & Luss, 1976; Huang & Varma, 1981a,b; Singh & Shah, 1982; Vleeschhouwer, Garton & Fortuin, 1992) dealt with the (dynamic) behaviour of gas–liquid processes. In none of these papers is a general applicable methodology presented to predict the dynamic behaviour of gas–liquid reactors.

Huang and Varma (1981a) treat the dynamic behaviour of gas–liquid reactions in non-adiabatic stirred tank

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reactors. Unfortunately, this paper is only applicable for the specific case of pseudo-first-order gas–liquid reactions in the so called fast reaction regime. For this specific case the key features of the system can be described by two ODEs (a gas-phase material and an overall heat balance) and a technique similar to that for single-phase reactors can be applied to investigate the dynamic behaviour. Vleeschhouwer et al. (1992) treat the analysis of the dynamic behaviour of an industrial oxo reactor. However, this gas–liquid process is also described by only one material balance of the liquid-phase component and a heat balance of the liquid-phase. The gas-phase components are not taken into account at all. This means that the process is simplified to a pseudo-first-order single phase reacting system. This implies constant liquid-phase concentrations of the gas-phase components which is strictly only valid for systems with a completely saturated liquid-phase (slow reaction regime and not too large Hinterland ratios (see Westerterp, van Swaaij & Beenackers, 1990)).

In the current paper two new models are introduced: (1) a rigorous model that can accurately describe the dynamic behaviour of gas–liquid reactors over a wide range of conditions and (2) an approximate model that can be used to obtain design rules for stable operation of gas–liquid reactors.

The rigorous model simultaneously solves the Higbie penetration model (partial differential equations) and the gas-phase and liquid-phase material balances (ODEs) for all components. Moreover, the heat balances for both phases are taken into account on macro as well as on micro scale. The model is an improved (non-isothermal) version of the model presented and validated in detail elsewhere (van Elk, Borman, Kuipers & Versteeg, 1999).

Using the rigorous model it is shown that the phenomenon limit cycle (dynamic instability) found for single phase reactors can also exist in gas–liquid reactors, even if mass transfer limitations are important. Generally these sustained oscillations have to be avoided, because they may adversely affect product quality and downstream operations and can lead to serious difficulty in process control and to unsafe operations. It is shown that the design rules of Vleeschhouwer et al. (1992) are not generally applicable for gas–liquid reacting systems. The rigorous model has one major disadvantage: it is not suited to create a so-called stability map that characterises the dynamic behaviour of the system as a function of certain selected system parameters.

The approximate prediction is however suited to create such stability maps from which design rules can be obtained. Our approximate method is more general than the design rules presented by Huang and Varma (1981) or Vleeschhouwer et al. (1992). The rigorous model, which takes into account all relevant phenomena, is still required in order to check the approximate results for a chosen set of operating conditions.

2. Theory

2.1. Introduction

The problem considered is a dynamic gas–liquid reactor with mass transfer followed by an irreversible second order chemical reaction:

$$A(g) + \gamma_b B(l) \rightarrow \gamma_c C(l) + \gamma_d D(l) \tag{1}$$

with the following overall reaction rate equation:

$$R_a = k_{R0,1,1} e^{-E_{act}/RT} [A][B]. \tag{2}$$

The mathematical models used are based on the following assumptions:

1. The mass transfer in the gas phase is described with the stagnant film model.
2. The mass transfer in the liquid phase is described with the penetration model.
3. The contact time according to the penetration model is small compared to the liquid-phase residence time.
4. Both the gas and the liquid-phase are assumed to be perfectly mixed (i.e. CISTRs).
5. The reaction takes place in the liquid-phase only.
6. The liquid-phase components (B,C and D) are non-volatile.

2.2. Rigorous model

For the penetration model the phenomenon of mass transfer accompanied by a chemical reaction is governed by the following equations for mass and heat:

$$\frac{\partial [A]}{\partial t} = D_a \frac{\partial^2 [A]}{\partial x^2} - R_a, \tag{3}$$

$$\frac{\partial [B]}{\partial t} = D_b \frac{\partial^2 [B]}{\partial x^2} - \gamma_b R_a, \tag{4}$$

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho_l C_{P,l}} \frac{\partial^2 T}{\partial x^2} + R \frac{\Delta H_R}{\rho_l C_{P,l}}. \tag{5}$$

To permit an unique solution of the non-linear partial differential equations (3)–(5) one initial Eq. (6) and two boundary conditions (7) and (8) are required

$$t = 0 \text{ and } x \geqslant 0\text{: } [A] = [A]_{l,\text{bulk}}, [B] = [B]_{l,\text{bulk}},$$
$$T = T_{l,\text{bulk}}, \tag{6}$$

$$t > 0 \text{ and } x = \delta_p\text{: } [A] = [A]_{l,\text{bulk}}, [B] = [B]_{l,\text{bulk}},$$
$$T = T_{l,\text{bulk}}, \tag{7}$$

$$J_a = -D_a\left(\frac{\partial[A]}{\partial x}\right)_{x=0} = k_g\left([A]_{g,\text{bulk}} - \frac{[A]_{x=0}}{m_a}\right),$$

$$\left(\frac{\partial[B]}{\partial x}\right)_{x=0} = 0, \tag{8}$$

$$J_T = -\lambda\left(\frac{\partial T}{\partial x}\right)_{x=0} = h_g(T_{g,\text{bulk}} - T_{x=0}).$$

The material and energy balances describing the system on macro scale are

$$\frac{\mathrm{d}[A]_{g,\text{bulk}}}{\mathrm{d}t} = \frac{[A]_{g,\text{in}} - [A]_{g,\text{bulk}}}{\tau_g} - \frac{J_a a}{\varepsilon_g}, \tag{9}$$

$$\frac{\mathrm{d}T_g}{\mathrm{d}t} = \frac{T_{g,\text{in}} - T_g}{\tau_g} - \frac{J_T a}{\rho_g C_{P,g}\varepsilon_g}, \tag{10}$$

$$\frac{\mathrm{d}[A]_{l,\text{bulk}}}{\mathrm{d}t} = \frac{[A]_{l,\text{in}} - [A]_{l,\text{bulk}}}{\tau_l} + \frac{J_a a}{\varepsilon_l} - R_{a,\text{bulk}}, \tag{11}$$

$$\frac{\mathrm{d}[B]_{l,\text{bulk}}}{\mathrm{d}t} = \frac{[B]_{l,\text{in}} - [B]_{l,\text{bulk}}}{\tau_l} - \gamma_b R_{a,\text{bulk}}, \tag{12}$$

$$\frac{\mathrm{d}T_l}{\mathrm{d}t} = \frac{T_{l,\text{in}} - T_l}{\tau_l} + \frac{J_T a}{\rho_l C_{P,l}\varepsilon_l} - \frac{UA(T_l - T_{\text{cool}})}{\rho_l C_{P,l}\varepsilon_l V_R} - \frac{R\Delta H_R}{\rho_l C_{P,l}}. \tag{13}$$

The overall rigorous mathematical model (see Fig. 1) combines the micro and macro model equations (3)–(13) by simultaneously solving the micro and macro model. The macro model is coupled to the micro model by the boundary conditions. The isothermal version of the model is described and validated in detail elsewhere (van Elk et al., 1999).

According to the penetration model a liquid element is exposed at the gas–liquid interface for a period θ during which mass transfer and accompanying chemical transformation takes place. Subsequently, the element is instantaneously swept to the ideally mixed liquid bulk and replaced by a new fresh one. The dimensions of the liquid element are assumed to be infinite compared to the penetration depth δ_p and therefore no direct mass and heat transport to the liquid bulk via the liquid element occurs

$$\frac{\mathrm{d}[A]_{l,\text{bulk}}}{\mathrm{d}t} = \frac{[A]_{l,\text{in}} - [A]_{l,\text{bulk}}}{\tau_l} - R_{a,\text{bulk}}. \tag{14}$$

The liquid-phase concentration directly after the element has been swept to the ideally mixed liquid bulk is:

$$[i]_l = \frac{N_{i,\text{elem}} + N_{i,\text{bulk}}}{\varepsilon_l V_R}. \tag{15}$$

The numerator represents the amount of moles present in the liquid phase after the contact time θ (see Fig. 1):

$$N_{i,\text{elem}} + N_{i,\text{bulk}} = [i]_{\text{bulk}}\varepsilon_l V_R + \int_0^{\delta_p}([i] - [i]_{\text{bulk}})\,\mathrm{d}x a V_R. \tag{16}$$

For the heat balance a similar procedure is used.

2.3. Simple model (2 ODEs) and perturbation analysis

The question arises whether or not the stability of gas–liquid reactors can be predicted without having to completely solve the complicated and time-consuming rigorous reactor model presented in the previous section. This is interesting for two reasons: (1) the rigorous reactor model requires much computational efforts and (2) the rigorous reactor model investigates only one set of conditions at a time, while predictive methods (like the so called perturbation analysis) result in a stability map that indicates the dynamic behaviour as a function of two chosen parameters. So, if a sufficiently accurate approximate prediction method could be derived this would be very attractive.

Vleeschhouwer et al. (1992) successfully predicted the dynamic system behaviour and the transition from a limit cycle to a point-stable steady state of a commercial scale gas–liquid oxo reactor using the so-called perturbation analysis. Analytical solution of the perturbation analysis is restricted to systems that can be described by two ODEs. The analysis involves linearisation of the governing non-linear ODEs in the neighbourhood of the steady state

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix}\partial x_1\\ \partial x_2\end{bmatrix} = \mathbf{A}\begin{bmatrix}\partial x_1\\ \partial x_2\end{bmatrix} \quad \text{with } \mathbf{A} = \begin{bmatrix}\dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2}\\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2}\end{bmatrix}_{\substack{x1=x1s\\ x2=x2s}}, \tag{17}$$

where x_1 and x_2 represent the perturbed concentration and temperature, respectively, in the case study of Vleeschhouwer et al. (1992). The functions f_1 and f_2 represent the right-hand sides of the mass and heat balance, where x_{1s} and x_{2s} represent the steady-state values of the concentration and temperature, respectively. A system is considered point-stable if, after a sufficiently small perturbation from the steady state, the system returns to its initial state.

A sufficient and necessary condition for a point-stable steady state is that the slope condition ($\det \mathbf{A} > 0$) as well as the dynamic condition ($\text{trace } \mathbf{A} < 0$) are fulfilled (in fact, this means that both eigenvalues of the linearised system must have negative real parts). If the slope condition is violated ($\det \mathbf{A} < 0$) the system shows static

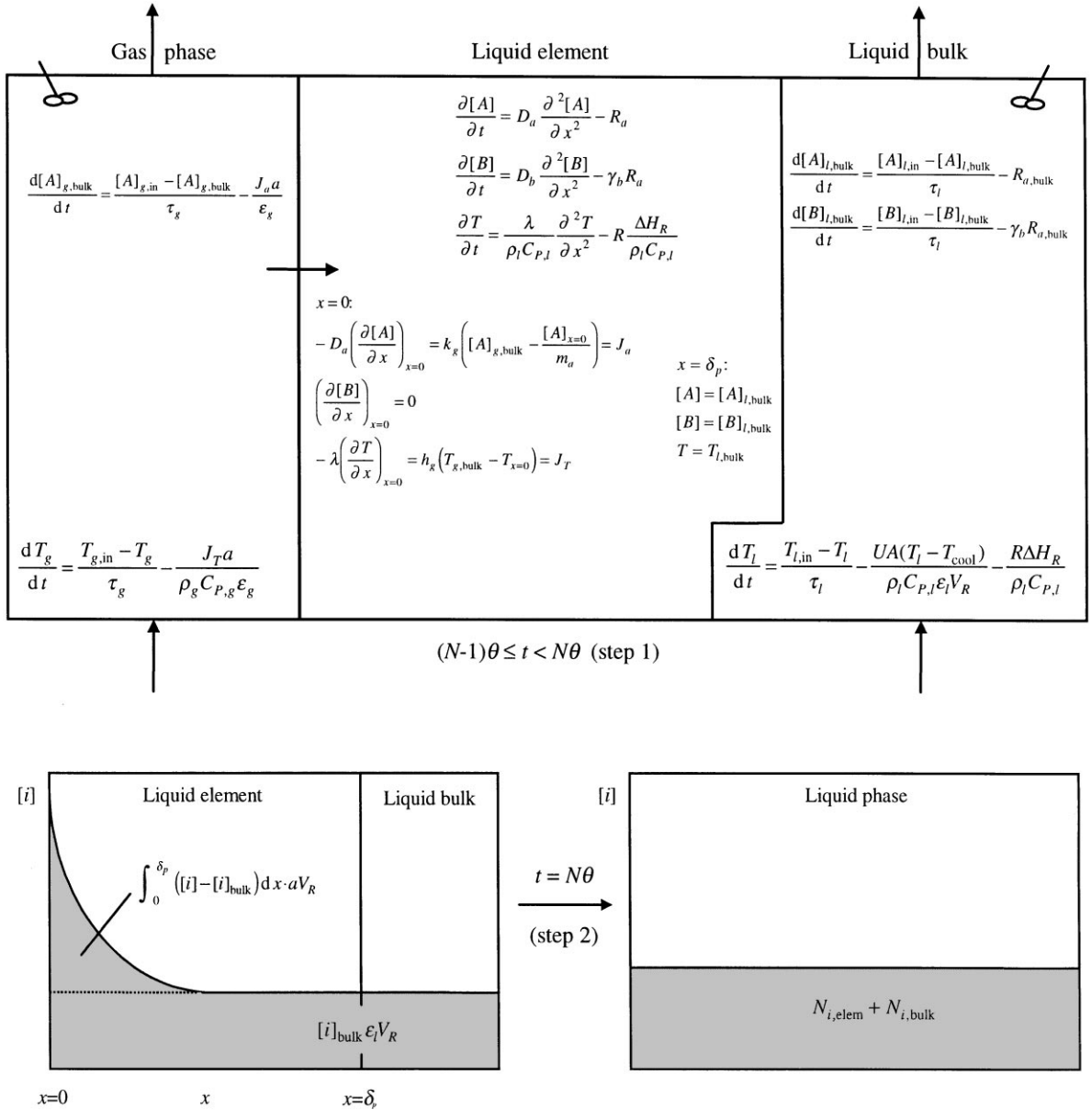

Fig. 1. The rigorous reactor model.

instability (extinction or ignition to a static stable point). If the dynamic condition is violated (trace $\mathbf{A} > 0$) the system shows dynamic instability (limit cycle).

If a plot (stability map) is made with S-shaped curves of the loci of points representing the steady states of the system as a function of a certain parameter (for example the coolant temperature), two additional curves can be drawn to divide the figure in three distinct regions, each with a characteristic dynamic behaviour. The two curves are the fold bifurcation curve (det $\mathbf{A} = 0$) and the Hopf bifurcation curve (trace $\mathbf{A} = 0$). The fold bifurcation curve is also known as the saddle-node bifurcation or slope curve. The three distinct regions are: I. region with point-stable steady states; II. region with dynamic instability (also called orbitally stable region or limit cycle region); III. region with static instability.

Thus, the perturbation analysis requires simplification of the overall reactor model to a system with only two ODEs. Most obvious is to reduce the system description to a system of equations that only includes one heat and one material balance. Vleeschhouwer et al. (1992) reduced their system to the following set:

$$\frac{d[B]_{l,bulk}}{dt} = \frac{[B]_{l,in} - [B]_{l,bulk}}{\tau_l} - \gamma_b R_{a,bulk}, \tag{18}$$

$$\frac{dT_l}{dt} = \frac{T_{l,in} - T_l}{\tau_l} - \frac{UA(T_l - T_{cool})}{\rho_l C_{P,l} \varepsilon_l V_R} - \frac{R\Delta H_R}{\rho_l C_{P,l}} \tag{19}$$

which implies that a constant value for $[A]_{l,\mathrm{bulk}}$ had to be assumed to enable calculation of the reaction rate. It seems reasonable to choose the steady-state value for this.

2.4. Approximate model (3 ODEs) and bifurcation analysis

The perturbation analysis presented by Vleeschhouwer et al. (1992), as described in Section 2.3, fails for systems in which mass transfer limitations are important. In this section an extension of their theory to these systems will be described. This new approximate method requires simplification of the rigorous reactor model to a system of ODEs and algebraic equations (AEs) only. The proposed system of ODEs is:

$$\frac{\mathrm{d}[A]_{l,\mathrm{bulk}}}{\mathrm{d}t} = \frac{-[A]_{l,\mathrm{bulk}}}{\tau_l} + \frac{k_l E_a a}{\varepsilon_l}(m_a[A]_g - [A]_{l,\mathrm{bulk}}) - R_{a,\mathrm{bulk}}, \tag{20}$$

$$\frac{\mathrm{d}[B]_{l,\mathrm{bulk}}}{\mathrm{d}t} = \frac{[B]_{l,\mathrm{in}} - [B]_{l,\mathrm{bulk}}}{\tau_l} - \gamma_b R_{a,\mathrm{bulk}}, \tag{21}$$

$$\frac{\mathrm{d}T_l}{\mathrm{d}t} = \frac{T_{l,\mathrm{in}} - T_l}{\tau_l} - \frac{UA(T_l - T_{\mathrm{cool}})}{\rho_l C_{P,l} \varepsilon_l V_R} - \frac{R\Delta H_R}{\rho_l C_{P,l}}. \tag{22}$$

Depending on the required accuracy and the reactor system considered, more ODEs can be added, for example if the reaction is reversible or if the gas phase has to be taken into account, too.

The model requires an algebraic expression (AE) for the enhancement factor to replace the micro model. The fact that the micro and macro balances are no longer solved simultaneously and that the mass and heat balances are decoupled on micro scale makes the model an approximate model. Van Swaaij and Versteeg (1992) concluded in their review that no generally valid approximate expressions are available to cover all gas–liquid processes accompanied with complex (reversible) reactions. However, for some asymptotic situations these expressions are available. For the present study we assumed that the reaction is irreversible and obeys first-order kinetics with respect to A and B. Then the following approximate relation can be used for estimating the enhancement factor:

$$E_a = \frac{E_{a,PS}^2}{2(E_{a_\infty} - 1)}\left\{\left[1 + 4\frac{(E_{a_\infty} - 1)}{E_{a,PS}^2}\right]^{0.5} - 1\right\}, \tag{23}$$

where

$$E_{a_\infty} = \sqrt{\frac{D_a}{D_b}} + \sqrt{\frac{D_b}{D_a}}\frac{[B]_{l,\mathrm{bulk}}}{\gamma_b [A]_l^i},$$

$$E_{a,PS} = Ha\left[\left\{1 + \frac{\pi}{8Ha^2}\right\}\mathrm{erf}\left[\sqrt{\frac{4Ha^2}{\pi}}\right] + \frac{1}{2Ha}\exp\left(\frac{4Ha^2}{\pi}\right)\right], \tag{24}$$

$$Ha = \frac{\sqrt{k_R [B]_{l,\mathrm{bulk}} D_a}}{k_l}.$$

For systems for which no approximate expression of the enhancement factor is available, a polynomial fit of data obtained by separate calculations of the rigorous reactor model can be implemented.

Creating a stability map of the system described by Eqs. (20)–(24) by the analytical perturbation analysis is not possible. However, bifurcation software packages like LOCBIF or AUTO can create a stability map for the system using a numerical bifurcation technique. Implementation of Eqs. (20)–(24) in bifurcation software (LOCBIF) results in a new and general prediction method. This method is very powerful for attaining design rules for stable operation of gas–liquid reactors.

LOCBIF is a software package that has the numerical routines to explore the existence and stability of equilibria in dynamical models with limited efforts.

3. Results

3.1. Introduction

To demonstrate the applicability of the models described in the previous sections, six fictitious but realistic cases were used. The values of important parameters used in the simulations are presented in Tables 1 and 2.

It is assumed that the gas-phase concentration remains constant and additionally that the contribution of the gas phase to the overall heat balance can be neglected. For systems where these additional assumptions are not valid, gas-phase conservation equations should be supplemented to the approximate model.

The odd cases (1, 3 and 5) refer to dynamically unstable and the even cases (2, 4 and 6) refer to dynamically stable conditions. Cases 1 and 2 are mainly controlled by the rate of the reaction kinetics ($Ha = 0.24$), while cases 3 and 4 ($Ha = 2.9$) and cases 5 and 6 ($Ha = 63.3$) are controlled by mass transfer processes.

Including the work of Vleeschhouwer et al. (1992) these cases cover the whole range from pre-mixed feed bulk reaction characterised by $(Al-1)Ha^2 \ll 1$ till fast film reaction with $(Al-1)Ha^2 \gg 1$. The physical meaning of $(Al-1)Ha^2$ is the ratio of the maximum conversion in the liquid bulk to the maximum transport through the mass transfer film (Westerterp et al., 1990). Vleeschhouwer et al. (1992) had a system with $(Al-1)Ha^2 \ll 1$, for cases 1 and 2 we have a system with $(Al-1)Ha^2 \approx 1$, for

Table 1
Fixed parameters used for all simulations

Case	$A(g) \rightarrow A(l)$, $A(l) + B(l) \rightarrow P(l)$ $R_a = k_{R,1,1}[A][B]$
$k_{R0,1,1}$	500,000
E_{act}	90,000 J mol^{-1}
R	8.314 J mol^{-1}K^{-1}
k_l	3.5×10^{-5}m s^{-1}
k_g	100 m s^{-1}(no gas resistance)
D_a	10^{-9}m^{2}s^{-1}
D_b	10^{-9}m^{2}s^{-1}
m_a	1.0
V_R	10 m^3
ε_l	0.5
a	1000 m^{2}m^{-3}
$\Phi_{l,\text{in/out}}$	0.005 m^{3}s^{-1}
ρ_l	800 kg m^{-3}
$C_{P,l}$	2000 J kg^{-1}K^{-1}
λ	0.02 W m^{-1}K^{-1}
ΔH_R	$-$ 160,000 J mol^{-1}
$T_{l,\text{in}}$	303 K

cases 3 and 4 we have $(Al-1)Ha^2 = 140$ and for cases 5 and 6 finally $(Al-1)Ha^2 \gg 1$.

3.2. Case 1 and 2 (*rigorous model*)

Solving the rigorous reactor model presented in Section 2.2 requires simultaneous solution of a set of coupled non-linear ordinary and partial differential equations (see Fig. 1) and results in the change of temperature and concentration in time. The change of the reactor temperature T_l in time for the parameter values of cases 1 and case 2 given in Tables 1 and 2 is shown in Fig. 2. Case 1 results in a limit cycle (dynamic unstable steady state) whereas case 2 results in a point-stable steady state.

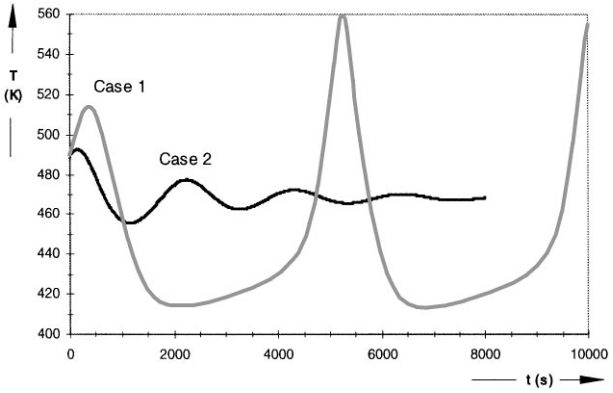

Fig. 2. Solution of the rigorous reactor model. $Ha = 0.24$, $(Al-1)Ha^2 = 0.94$, $T_s = 468$ K. Case 1: $UA = 35{,}000$ and case 2: $UA = 55{,}000$.

3.3. Cases 1 and 2 (*simple model*)

A stability map, obtained by a perturbation analysis of Eqs. (18) and (19) using the data of cases 1 and 2 and $[A]_{l,\text{bulk}} = 50.1$ mol m^{-3} (the steady-state value, see Table 2) is given in Fig. 3. From the stability map it can be seen that for both cases 1 and 2 a limit cycle is predicted (region II). From Fig. 2 it can however be seen that this does not agree with the results obtained from the rigorous reactor model developed in the present study. In Fig. 4 the solution of the simple model is given and it can be seen that this does indeed show a limit cycle for case 2, as predicted.

It can thus be concluded that the perturbation analysis does agree with the results of the simple model, but apparently the simple model fails for complex processes. This means that the perturbation analysis as presented by Vleeschhouwer et al. (1992) is not generally applicable

Table 2
Operating conditions and initial values used and the corresponding steady state values (approximate model)

Case	Cases 1 and 2	Cases 3 and 4	Cases 5 and 6
$[A]_{g,\text{bulk}}$	100 mol m^{-3}	100 mol m^{-3}	5.0 mol m^{-3}
$[B]_{l,\text{in}}$	5000 mol m^{-3}	25,000 mol m^{-3}	25,000 mol m^{-3}
T_{cool}	425 and 441 K	469 and 507 K	673 and 715 K
UA	35,000 and 55,000 W K^{-1}	150,000 and 250,000 W K^{-1}	75,000 and 100,000 W K^{-1}
Regime	Kinetics controlled/intermediate	Mass transfer controlled	Mass transfer controlled
Ha_s	0.24	2.9	63.3
$(Al-1)Ha^2$	0.94 ($\approx$ 1.0)	140 ($>$ 1.0)	66,074 ($\gg$ 1.0)
T_s	468 K	565 K	842 K
T_0	488 K (step disturbance 20°C)	575 K (step disturbance 10°C)	852 K (step disturbance 10°C)
$[A]_{l,\text{bulk},s}$	50.1 mol m^{-3}	2.0 mol m^{-3}	0.004 mol m^{-3}
$[B]_{l,\text{bulk},s}$	1558 mol m^{-3}	4354 mol m^{-3}	3760 mol m^{-3}
$UA_{\text{design rule}}$	$>$ 50,418 W/K (Fig. 5)[a]	$>$ 214,848 W/K (Fig. 7)[a]	$>$ 98,934 W/K (Fig. 10)[a]
$T_{\text{cool, design rule}}$	$>$ 438 K (Fig. 5)*	$>$ 509 K (Fig. 7)[a]	$>$ 693 K (Fig. 10)[a]

[a]If one of these two design rules is fulfilled the system will show point stable steady states.

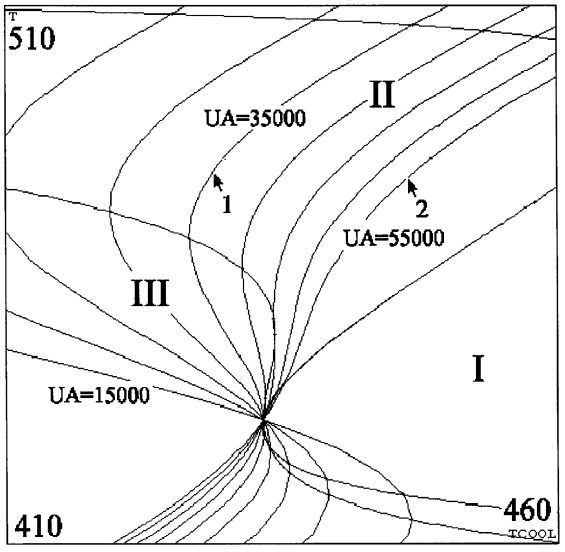

Fig. 3. Stability map of the simple reactor model (2 ODEs). The steady state temperature is plotted as a function of the cooling temperature and the heat transfer parameter UA. The points 1 and 2 refer to cases 1 and 2 from Table 2. Regions I, II and III refer to point stable, limit cycle and static unstable conditions, respectively.

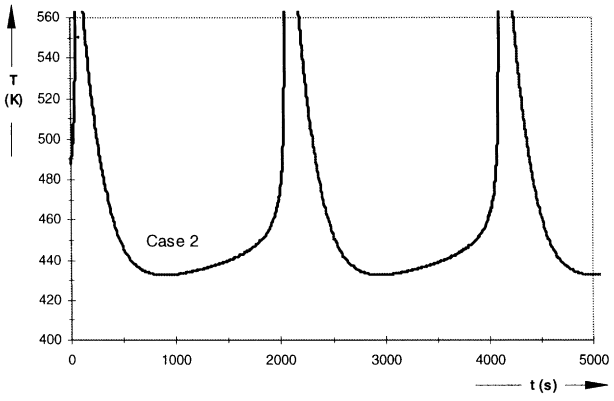

Fig. 4. Solution of the simple reactor model (2 ODEs). $Ha = 0.24$, $(Al-1)Ha^2 = 0.94$, $T_s = 468$ K. Case 2: $UA = 55{,}000$.

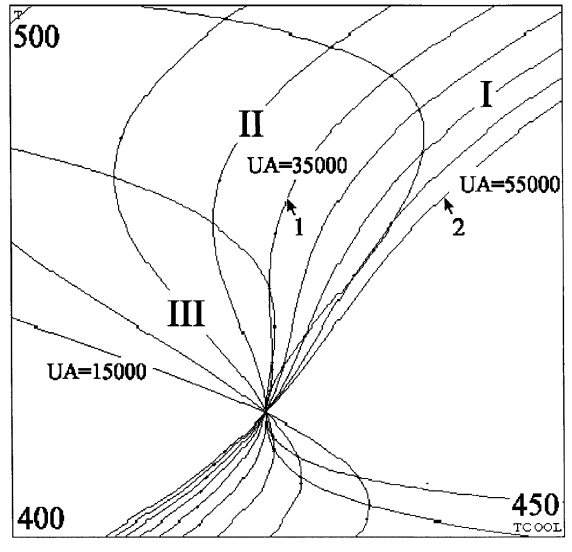

Fig. 5. Stability map of the approximate reactor model (3 ODEs). The steady state temperature is plotted as a function of the cooling temperature and the heat transfer parameter UA. Points 1 and 2 refer to cases 1 and 2 from Table 2. Regions I, II and III refer to point stable, limit cycle and static unstable conditions, respectively.

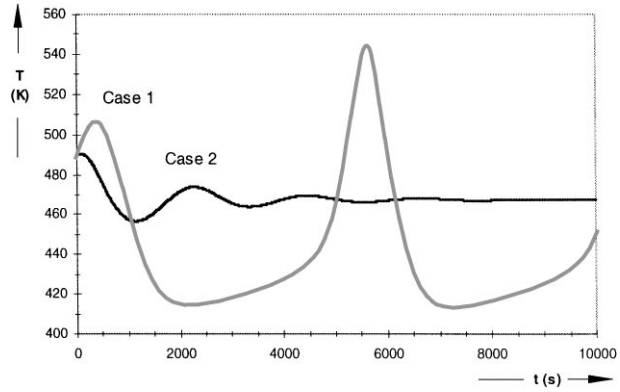

Fig. 6. Solution of the approximate reactor model (3 ODEs). $Ha = 0.24$, $(Al-1)Ha^2 = 0.94$, $T_s = 468$ K. Case 1: $UA = 35{,}000$ and case 2: $UA = 55{,}000$.

and only valid for the specific case of systems with a completely saturated liquid phase ($(Al-1)Ha^2 \ll 1$, see Westerterp et al., 1990).

3.4. *Cases 1 and 2* (*approximate model*)

A stability map, obtained by a bifurcation analysis of Eqs. (20)–(24) was created using the LOCBIF bifurcation software package. From the stability map (Fig. 5) it is predicted that case 1 is a limit cycle and case 2 is point-stable, which corresponds with the results of the rigorous model. From the stability map the following design rule is obtained for this specific system: as long as either UA is larger than 50,418 W/K or T_{cool} is larger than 438 K the steady states are point stable (region I).

The solution of the system of Eqs. (20)–(24) for cases 1 and 2 is shown in Fig. 6. Comparing Fig. 2 (rigorous reactor model) and Fig. 6 (approximate model) shows that the approximate model with 3 ODEs (20)–(22) and 1 AE (Eq. (24) substituted in Eq. (23)) gives reasonable results.

3.5. *Cases 3 and 4* (*rigorous and approximate model*)

Cases 1 and 2 used for the calculations presented in the previous sections correspond to systems that are mainly controlled by the reaction kinetics ($Ha = 0.24$). In this section it will be shown that the bifurcation analysis based on the approximate (3 ODEs) model is also applicable in the mass transfer controlled regime ($Ha > 2.0$).

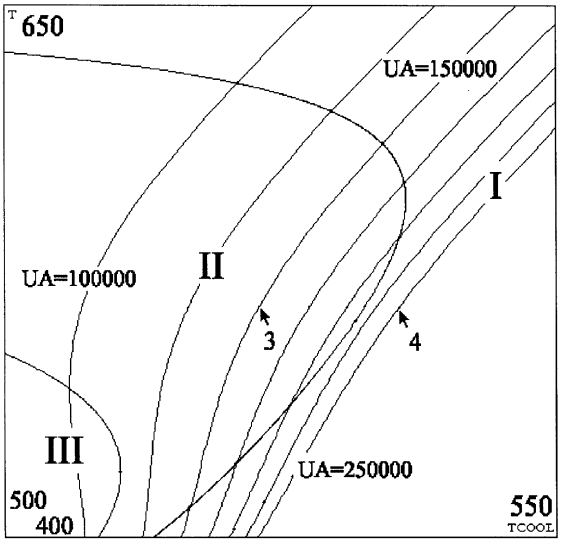

Fig. 7. Stability map of the approximate reactor model (3 ODEs). The steady state temperature is plotted as a function of the cooling temperature and the heat transfer parameter UA. The points 3 and 4 refer to cases 3 and 4 from Table 2. Regions I, II and III refer to point stable, limit cycle and static unstable conditions, respectively.

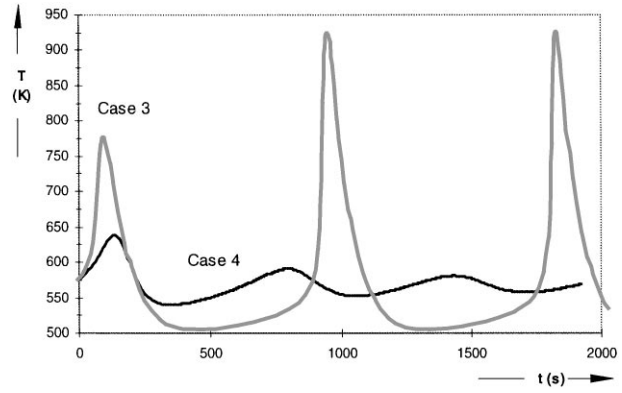

Fig. 8. Solution of the rigorous reactor model. $Ha = 2.9$, $(Al-1)Ha^2 = 140$, $T_s = 565$ K. Case 3: $UA = 150{,}000$ and case 4: $UA = 250{,}000$.

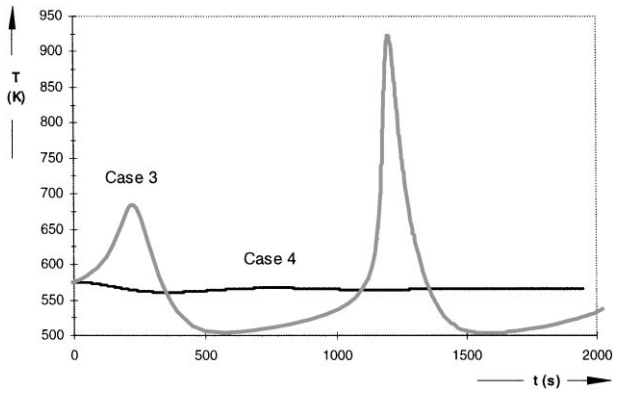

Fig. 9. Solution of the approximate reactor model (3 ODEs). $Ha = 2.9$, $(Al-1)Ha^2 = 140$, $T_s = 565$ K. Case 3: $UA = 150{,}000$ and case 4: $UA = 250{,}000$.

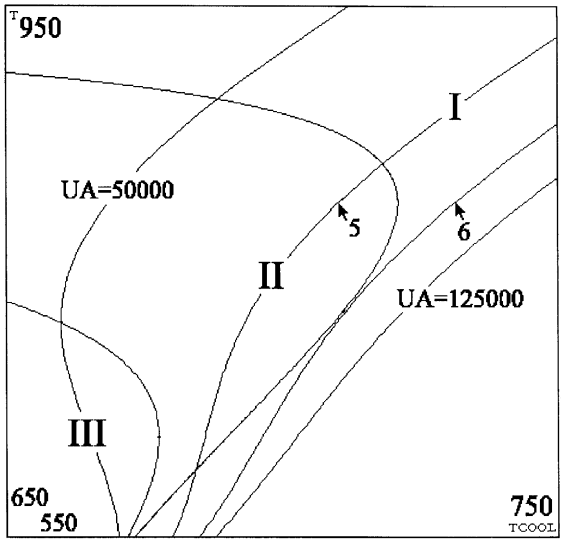

Fig. 10. Stability map of the approximate reactor model (3 ODEs). The steady state temperature is plotted as a function of the cooling temperature and the heat transfer parameter UA. The points 5 and 6 refer to cases 5 and 6 from Table 2. Regions I, II and III refer to point stable, limit cycle and static unstable conditions, respectively.

This is done by appropriate modification of the conditions (cases 3 and 4 defined in Table 2).

A stability map, obtained by a bifurcation analysis using LOCBIF and the approximate model, is shown in Fig. 7. It is predicted that case 3 is a limit cycle and case 4 is point-stable. From Fig. 8 it can be seen that this corresponds with the results obtained from the rigorous model. The exact design rules for point stable steady states are given in Table 2.

Fig. 9 shows the solution of the approximate model. Comparing Figs. 8 and 9 shows some discrepancy between the approximate and the rigorous model. This is most probably caused by the fact that the approximate model does not take the temperature profile on micro scale into account (Vas Bhat et al., 1997). Moreover, for these cases the heat of reaction is produced mainly in the mass transfer film near the gas–liquid interface, contrary to the approximate rigorous method which assumes bulk heat generation.

3.6. Cases 5 and 6 (*rigorous and approximate model*)

Cases 3 and 4 are mainly controlled by mass transfer ($Ha = 2.9$, $(Al-1)Ha^2 = 140$), but the concentration of the gas-phase component A in the liquid bulk is not yet completely zero ($[A]_{l,\mathrm{bulk}} = 2.0$ mol m^{-3}). Cases 5 and 6 are characterised by a very fast reaction ($Ha = 63.3$, $(Al-1)Ha^2 \gg 1$), so that the liquid bulk is fully depleted

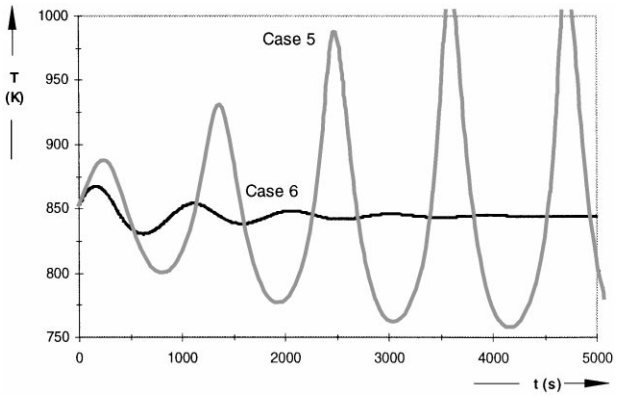

Fig. 11. Solution of the rigorous reactor model. $Ha = 63.3$, $(Al-1)Ha^2 = 66074$, $T_s = 842$ K. Case 5: $UA = 75{,}000$ and case 6: $UA = 100{,}000$.

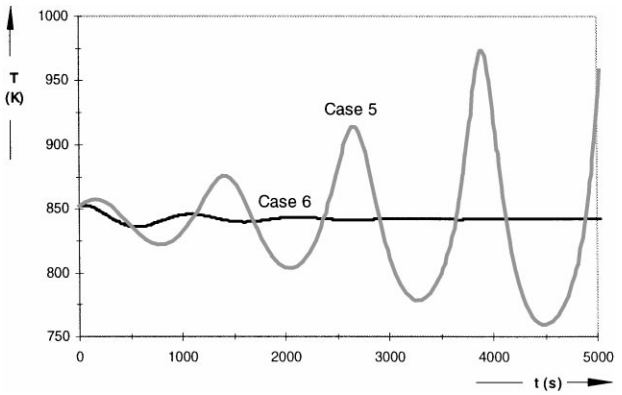

Fig. 12. Solution of the approximate reactor model (3 ODEs). $Ha = 63.3$, $(Al-1)Ha^2 = 66074$, $T_s = 842$ K. Case 5: $UA = 75{,}000$ and case 6: $UA = 100{,}000$.

($[A]_{l,\text{bulk}} = 0.004$ mol m^{-3}). This is achieved by appropriate modification of the conditions (Table 2).

A stability map, obtained by using the approximate model is shown in Fig. 10. It is predicted that case 5 is a limit cycle and case 6 is point-stable. From Figs. 11 and 12 it can be seen that this corresponds with the results obtained from the rigorous model and the approximate model, respectively. The exact design rules for point stable steady states are given in Table 2. Comparing Figs. 11 and 12 shows again some discrepancy between the approximate and the rigorous model.

4. Conclusions

A rigorous model is presented that can accurately describe the dynamic behaviour of ideally stirred gas–liquid reactors over a wide range of conditions. The model is used to demonstrate the possible existence of limit cycles in gas–liquid processes.

It is concluded (see Table 3, simple model) that the perturbation analysis from Vleeschhouwer et al. (1992) is not generally applicable for prediction of the dynamic behaviour of ideally stirred gas–liquid processes. Application of these design rules is restricted to systems with a fully saturated liquid phase ($(Al-1)Ha^2 \ll 1$, see Westerterp et al. (1990)).

The new approximate model presented in this paper gives more general applicable results and covers the complete region from pre-mixed feed bulk reaction ($(Al-1)Ha^2 \ll 1$) to fast film reaction ($(Al-1)Ha^2 \ll 1$). A bifurcation analysis based on this model is a powerful and general tool to obtain design rules for stable operation of ideally stirred gas–liquid reactors.

The decoupling of mass and heat balances on micro scale increases the error of the approximate model and the corresponding bifurcation analysis (especially in the fast reaction regime). Therefore, the rigorous reactor model should be used to check the obtained design rules and to investigate the dynamic system behaviour in more detail.

Notation

a	specific surface area, m^2 m^{-3}
A	heat transfer area, m^2

Table 3
Overview of the results.

Case	T_{cool}	UA	T_s	Rigorous	Simple model (2 ODE)		Approximate model (3 ODE)	
	(K)	(W/K)	(K)	model	Solution of model	Perturbation analysis	Solution of model	Bifurcation analysis
1	425	35,000	468	Limit cycle	Limit cycle	Limit cycle	Limit cycle	Limit cycle
2	441	55,000	468	Point stable	Limit cycle	Limit cycle	Point stable	Point stable
3	469	150,000	565	Limit cycle			Limit cycle	Limit cycle
4	507	250,000	565	Point stable			Point stable	Point stable
5	673	75,000	842	Limit cycle			Limit cycle	Limit cycle
6	715	100,000	842	Point stable			Point stable	Point stable
		Conclusion →		Exact solution	Simple model fails		Approximate model succeeds	

$[A]$	concentration of component A
Al	Hinterland ratio (defined by $\varepsilon_l k_l/aD_o$),1
$[B]$	concentration of component B
$[C]$	concentration of component C
C_P	heat capacity, J kg^{-1} K^{-1}
$[D]$	concentration of component D
$D_{\text{subscript}}$	diffusivity, m^2 s^{-1}
E_{act}	activation energy, J mol^{-1}
$E_{\text{subscript}}$	enhancement factor, 1
h_g	gas-phase heat transfer coefficient, W m^{-2} K^{-1}
ΔH_R	heat of reaction based on R, J mol^{-1}
Ha	Hatta number defined as $\sqrt{(k_R[B]D_a/k_{l^2})}$,1
$J_{\text{subscript}}$	molar flux, mol m^{-2} s^{-1}
J_T	heat flux, W m^{-2}
k_g	gas-phase mass transfer coefficient, m s^{-1}
k_l	liquid-phase mass transfer coefficient, m s^{-1}
$k_{R,m,n}$	reaction rate constant, m$^{3(m+n-1)}$ mol$^{-(m+n-1)}$ s^{-1}
m	reaction order, 1
$m_{\text{subscript}}$	gas–liquid partition coefficient, 1
n	reaction order, 1
N	counter with start value 1 at $t = 0$, 1
$N_{\text{subscript}}$	number of moles, mol
$R_{\text{subscript}}$	reaction rate, mol m^{-3} s^{-1}
R_{gas}	ideal gas constant, J mol^{-1} K^{-1}
t	simulation time variable, s
T	temperature, K
U	heat transfer coefficient, W m^{-2} K^{-1}
V_R	reactor volume, m^3
x	place variable, m
$x_{\text{dimensionless}}$	place variable defined as $x/\sqrt{(4D_a\theta)}$,1
$[]$	concentration, mol m^{-3}
$[]_{\text{subscript}}$	concentration, mol m^{-3}

Greek letters

$\gamma_{\text{subscript}}$	stoichiometry number, 1
δ_p	assumed thickness of liquid element, m
ε_g	gas-phase hold-up, 1
ε_l	liquid-phase hold-up, 1
λ	thermal conductivity, W m^{-1} K^{-1}
ρ	density, kg m^{-3}
θ	contact time according to penetration model (defined by $4D_a/\pi k_l^2$), s
τ_l	liquid-phase residence time, s

Subscripts

0	initial value
a	component A
b	component B
bulk	at bulk conditions
c	component C
cool	cooling medium
d	component D
g	gas phase
i	interface
i	species i
in	at inlet conditions
l	liquid phase
s	steady-state value
T	temperature

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